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Highly flame resistant rigid urethane-isocyanurate foam compositions.

Highly flame resistant rigid urethane-isocyanurate foams, are prepared from compositions containing blowing agent, a polyester polyol derived from the residue of dimethyl terephthalate or terephthalic acid production, a phosphorus containing polyol and an isocyanurate catalyst, in which the NCO : OH ratio is 8 to 6.

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A CURABLE COMPOSITION FOR PRODUCING A FLAME  
RESISTANT URETHANE-ISOCYANURATE FOAM AND A FOAM  
PRODUCED FROM SUCH COMPOSITIONS

This invention is directed to compositions for the preparation of highly flame resistant rigid urethane-isocyanurate foams which meet the stringent class B1 requirements for the Flammability Test Method DIN-4102.

According to the invention, there is provided a composition available to a flame resistant polymer foam comprising:

- I. a blowing agent;
- II. a polyester polyol mixture prepared by:
  - a) transesterification, with a glycol of molecular weight from 60 to 400, of a residue remaining after dimethyl terephthalate and methyl p-toluate have been removed from the product of oxidation of p-xylene in the preparation of dimethyl terephthalate; or
  - b) esterification, with an alkylene oxide selected from ethylene oxide, propylene oxide, butylene oxide, and mixtures thereof, of a carboxyl functional residue resulting from the removal of terephthalic acid from the mixture obtained by the oxidation of p-xylene in the preparation of terephthalic acid;
- III. a phosphorus containing polyol;
- IV. a polymeric polyisocyanate;
- V. an isocyanurate catalyst in which the NCO:OH mole ratio is 3:1 to 6:1.

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In the above composition, the particular blowing agent I employed is not critical, although halogenated organic blowing agents are customarily used. Preferred blowing agents are trichlorofluoromethane and dichlorodifluoromethane.

The "residue" from which the polyester polyol component II is prepared is described in more detail in U.S. Patents 3,647,759 and 4,237,238. The residue is the product remaining after dimethyl terephthalate and methyl p-toluate have been removed from the product of oxidation of p-xylene in the preparation of dimethyl terephthalate. Alternatively, the residue can comprise the product remaining after the removal of terephthalic acid from the mixture obtained by the oxidation of p-xylene in the preparation of terephthalic acid. In the first case, the residue contains ester groups which are transesterified with a glycol such as ethylene glycol in order to prepare the polyester polyol. In the latter case, the residue contains carboxyl groups which can be esterified with an alkylene oxide such as ethylene oxide, propylene oxide or butylene oxide to prepare a similar polyester polyol mixture.

Suitable phosphorus containing polyols III include those disclosed in U.S. Patent 3,525,705. A particularly preferred phosphorus containing polyol is the propylene oxide adduct of dibutyl pyrophosphoric acid described in Example XI of said patent. The amount of phosphorus containing polyol III used is selected to achieve the desired Class BI flame resistance. Generally this amount corresponds to a weight ratio of polyester polyol II to phosphorus polyol of 4:1 to 10:1.

The polymeric polyisocyanates IV preferred for use herein are polymethylene poly(phenyl isocyanates) which are commercially available materials. The amount of polyisocyanate present should be selected so that the ratio of the isocyanate equivalents therein the total hydroxyl equivalents in components II and III is in the range of 3:1 to 6:1, more preferably in the range of 3:1 to 4:1.

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A variety of catalysts V which promote the formation of isocyanurate groups during the curing reaction are known and commercially available. For example, salts of higher fatty acids such as amine and potassium salts, e.g. potassium octoate, are suitable isocyanurate catalysts.

In addition, the curable composition may include a catalyst which promotes the formation of urethane groups, a variety of such urethane catalysts being known and commercially available.

An epoxide is also an optional ingredient which has been found to be beneficial in reducing foam shrinkage. Bisphenol epoxides, particularly those based on bisphenol A, available commercially are preferred. The epoxide is generally present in an amount of 2% or less.

The foam composition may also contain additional flame retardants, preferably organic compounds containing both halogen and phosphorus. Tris(beta-chloropropyl) phosphate is particularly preferred.

It has been found that the addition of non-ionic surfactants is often beneficial, although the maximum desirable addition is about 2 weight percent to prevent loss of desirable foam properties. Suitable surfactants are well known in the art.

The curable compositions disclosed herein are particularly useful for the preparation of rigid urethane-isocyanurate foams which meet the stringent requirements for a Class B1 rating under the Flammability Test method DIN-4102.

A representative foam composition in accordance with this invention is described in the example, in which all amounts are expressed in parts by weight unless otherwise stated.

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EXAMPLE

A mixture was prepared from 3,282 grams Terate 203<sup>1</sup>, 636.9 grams of the propylene oxide adduct of dibutyl pyrophosphoric acid (Example XI, U.S. 3,525,705), 134.6 grams Epon 828 (Shell Chemical Co. - an epoxide resin based on bis-phenol A), 91.9 grams DC-193 surfactant<sup>2</sup>, 105 grams polyisocyanurate catalyst X-798<sup>3</sup>, 55.8 grams dimethylethanolamine and 2,275.1 grams of trichloromonofluoromethane as a blowing agent. The mixture was stirred using a two blade, propeller stirrer operating at 1,500 RPM.

After replacing the blowing agent lost due to evaporation, 10,935.7 grams of polymethylene poly(phenyl isocyanate)<sup>4</sup> were added followed by vigorous agitation as above for 22 seconds. The mixture was poured into a 48" x 48" x 12" (122cm x 122cm x 30cm) cardboard box and was allowed to free rise. The homogenous mixture creamed after five seconds and was fully risen in 103 seconds.

The bun was allowed to stand at room temperature for 48 hours prior to trimming and cutting for flame testing according to the DIN-4102 test method.

The NCO/OH ratio of the above formulation was 4.0 and the flame retardant polyol concentration was 3.6% based on total formulation weight. A non-brittle foam was produced having a core density of 30 kg/M<sup>3</sup>.

A B1 rating was obtained when the above foam was tested by the DIN-4102 method at sample thickness of 40MM. The average of three tests showed 22 cm of unburned or uncharred sample and 148°C flue gas temperature, compared to B1 specifications of 15 cm minimum and 200°C maximum, respectively.

The several components used in the composition are specifically identified as follows:

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1. Terate 203 is commercially available from Hercules Inc. and is believed to be a product prepared by transesterification of the residue of a dimethyl terephthalate esterified oxidate reaction product with an excess of diethylene glycol, as described in U.S. Patent 3,647,759 and U.S. Patent 4,237,238.

2. DC 193 is a silicone surfactant commercially available from Dow Corning Chemical.

3. X-798 is an isocyanurate catalyst, commercially available from Air Products.

4. The polymeric polyisocyanate is a polymethylene poly(phenyl isocyanate) with an average functionality of about 2.5 and an NCO content of 32 percent.

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CLAIMS:

1. A composition curable to a flame resistant polymer foam comprising:
  - I. a blowing agent;
  - II. a polyester polyol prepared by
    - a) transesterification, with a glycol of molecular weight from about 60 to about 400, of a residue remaining after dimethyl terephthalate and methyl p-toluate have been removed from the product of oxidation of p-xylene in the preparation of dimethyl terephthalate; or
    - b) esterification, with an alkylene oxide selected from the group consisting of ethylene oxide, propylene oxide, butylene oxide, and mixtures thereof, of a carboxyl functional residue resulting from the removal of terephthalic acid from the mixture obtained by the oxidation of p-xylene in the preparation of terephthalic acid;
  - III. a phosphorus containing polyol;
  - IV. a polymeric polyisocyanate; and
  - V. an isocyanurate catalyst; wherein the NCO:OH mole ratio is 3:1 to 6:1.
2. The composition of claim 1 in which the NCO:OH mole ratio is 3:1 to 4:1.
3. The composition of claim 1 or claim 2 in which said phosphorus containing polyol III is a propylene oxide adduct of a di(lower alkyl) pyrophosphoric acid.
4. The composition of claim 3 in which said phosphorus containing polyol III is a propylene oxide adduct of a dibutyl pyrophosphoric acid.
5. The composition of any preceding claim in which said polymeric polyisocyanate IV is a polymethylene poly(phenyl isocyanate).

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6. The composition of any preceding claim which contains in addition a bisphenol epoxy resin.

7. The composition of any preceding claim in which the weight ratio of polyester polyol II to phosphorus containing polyol III is 4:1 to 10:1.

8. A rigid isocyanurate-urethane foam produced by curing a composition according to any preceding claim.

4939H/0299H



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## EUROPEAN SEARCH REPORT

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EP 84 30 8638

| DOCUMENTS CONSIDERED TO BE RELEVANT   |  |  |  |
|---|--|--|--|
| Category  | Citation of document with indication, where appropriate, of relevant passages                              | Relevant to claim  | CLASSIFICATION OF THE APPLICATION (Int. Cl.4)  |
| X   | EP-A-0 086 882 (CELOTEX)<br>* Page 5, lines 14-21; page 10, lines 7-13; claims 1-11 *                      | 1-8  | C 08 L 75/06<br>C 08 G 18/42   |
| D,Y   | US-A-4 237 238 (D.T. DEGUISEPPI et al.)<br>* Column 2, lines 11-27; examples 1-3; claims 1-7 *             | 1-8  |  |
| D,Y   | US-A-3 525 705 (C.L. HAROWITZ)<br>* Column 5, lines 43-57; column 14, lines 17-31; example 6; claims 1-8 * | 1-8  |  |
| A   | US-A-4 346 229 (L.K. DERR et al.)<br>* Column 3, lines 3-15; example 9; claim 1 *                          | 1  |  |
|   |  |  | TECHNICAL FIELDS SEARCHED (Int. Cl.4)  |
|   |  |  | C 08 G 18/30<br>C 08 G 18/42<br>C 08 L 71/02<br>C 08 L 75/04<br>C 08 L 75/06<br>C 08 L 75/08 |
| The present search report has been drawn up for all claims  |  |  |  |
| Place of search<br>BERLIN   |  | Date of completion of the search<br>25-03-1985   | Examiner<br>BOURGONJE A.F.   |
| CATEGORY OF CITED DOCUMENTS   |  | T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br>& : member of the same patent family, corresponding document |  |
| X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document |  |  |  |

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